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ATTEMPT TO EXPLAIN THE REACTION MECHANISM

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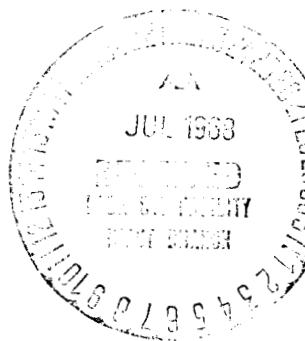
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THERMAL DISSOCIATION OF BASIC AMMONIUM ALUMINUM SULPHATE.
II. MEASUREMENTS OF THE DECOMPOSITION RATE AND ATTEMPT TO EXPLAIN THE REACTION MECHANISM

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ABSTRACT. The thermal dissociation rate of basic ammonium aluminum sulphate and partially decomposed preparations was studied. It was found that at temperatures of 300-400° C, the dehydration of the compound occurs in the kinetic range. At temperatures of 400-470°C (H_2O and NH_3 being driven off), the dissociation occurs in the diffusion range, and a further temperature rise (470-540°C) causes the reaction to pass to the kinetic range. Decomposition of the preparation from which H_2O and NH_3 have been removed takes place at temperatures of 780-860°C in the diffusion range. Above 860°C (up to 900°C), the kinetics determine the overall decomposition rate. The values of the apparent activation energies of certain steps of the dissociation are: at 470-540°C, 32.7; at 780-860°C, 45.7, and at 860-900°C, 63.0 kcal per mole.

STATUS OF THE PROBLEM /137*

Thus far, the thermal dissociation kinetics of basic ammonium aluminum sulphate have been discussed in only one paper (1). The authors studied the kinetics of decomposition in a fluidized bed by determining the temperatures of the successive stages of calcination (the temperature of the fluidization oven being slowly raised), the degree of calcination of the starting material as a function of time (and at a given temperature of the oven), the rate of /138 removal of ammonia at 403°C, and the change in the decomposition rate of the basic ammonium aluminum sulphate at a given temperature.

The kinetics and mechanism of thermal dissociation of the compound are unknown. The temperature dependence of the reaction rate and the mechanism of the process of separation of water, ammonia and sulphur trioxide are factors which determine the method of decomposition under industrial conditions.

The purpose of the present study was to determine the reaction rate of thermal dissociation of basic ammonium aluminum sulfate at atmospheric pressure in the 300-900°C range on the basis of earlier studies of the decomposition stages (2). The kinetic data obtained formed the basis for the elucidation of the mechanism of separation of water, ammonia and sulphur trioxide at different temperatures.

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*Numbers in the margin indicate pagination in the foreign text.

EXPERIMENTAL METHOD

The study of the decomposition rate was carried out gravimetrically (2).

Samples of basic ammonium aluminum sulphate and samples of partially decomposed preparations were placed in a platinum crucible and introduced into the constant temperature zone of an oven preheated to the temperature of the measurement. The temperature of the measurement chamber of the oven was measured with a PtRh-Pt thermocouple. The temperature was controlled to within ±1°C. The results of measurements of change in the weight of the sample as a function of the decomposition time were obtained in the form of tracings on paper tape.

The kinetic studies included three series of experiments:

I. Measurements of the decomposition rate of basic ammonium aluminum sulphate in the 300-540°C range.

II. Measurements of the decomposition rate of the partially dehydrated compound as a result of preliminary calcination for 8 hours at 320°C. These measurements were made at 430-540°C.

III. Measurements of the decomposition rate of the compound initially decomposed for 8 hours at 540°C. The measurements were made at 750-900°C.

Chemical analyses of basic ammonium aluminum sulphate studied in series I of the measurements show the following contents.

Al_2O_3 34.30-35.05%

SO_3 41.39-42.07%

NH_3 3.17- 3.25%

H_2O 19.63-21.11%

In series II of the measurements, a preparation of the composition Al_2O_3-36.44%, SO_3 - 43.83% and NH_3 - 3.2% was studied. The chemical composition of the preparation thus obtained corresponded approximately to the formula:

$$(NH_4)_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O,$$
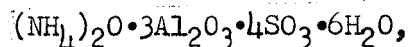
and the loss of about 4.5% of the weight indicated the removal of two water molecules.

The preparation studied in series III of the measurements had the following composition: Al_2O_3, 44.05%; SO_3, 53.17% and NH_3, 0.06%, which corresponded approximately to the overall formula:

$$3Al_2O_3 \cdot 4SO_3$$
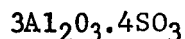
(and hence almost completely devoid of ammonia and water). The preparation

consisted of a mixture of anhydrous aluminum sulphate of the low-temperature modification of γ-Al$_2$O$_3$ having a partially preserved alunite structure (2).

RESULTS

Tables 1a and 1b and Figure 1 show the results of measurements of the decomposition rates of basic ammonium aluminum sulphate The results of the calculations contained in the tables are given in Figs. 2 and 3.

Table 1a. Results of Measurements at 350-540°C (I Series)

τ min.	Temperature 340° C			Temperature 400 C		
	w_τ	$1-\sqrt[3]{1-\alpha}$	k_1	w_τ	$1-\sqrt[3]{1-\alpha}$	k_1
2,5	0,7858	0,158	0,0632	0,7789	0,199	0,0786
5	0,7736	0,341	0,0682	0,7677	0,363	0,0727
7,5	0,7701	0,423	0,0564	0,7622	0,478	0,0638
10	0,7665	0,545	0,0545	0,7577	0,696	0,0696
12,5	0,7637	0,738	0,0591	0,7564	—	—
15	0,7630	—	—	—	—	—

$k_{1\text{śr}} = 0,0602$ $k_{1\text{śr}} = 0,0713$

mean error 7,15 %   mean error 6,25 %

maximum error 13,3 %   maximum error 10,5 %

In the second series of measurements (Tables 2a and 2b and Fig. 4), the thermal dissociation rate of previously dehydrated basic ammonium aluminum sulphate was determined. The results of calculations contained in Tables 2a and 2b are shown in Figs. 5 and 6, and the temperature dependence of the reaction rate constant obtained is shown in Fig. 7.

The results of measurements of the thermal dissociation rate of the preparation studied in series III of the measurements are given in Tables 3a and 3b and in Fig. 8. Figures 9 and 10 show results of calculations contained in Tables 3a and 3b. The temperature dependence of the rate constants k_1 and k_2 are shown in Fig. 11.

DISCUSSION AND CONCLUSIONS

The experimental results were processed by using the relations:

$$1-\sqrt[3]{1-\alpha} = k_1\tau, \tag{1}$$

$$1-\sqrt[3]{1-\alpha} = k_2\sqrt{\tau}, \tag{2}$$

$$1-\alpha = \exp(-k_3\tau^n), \tag{3}$$

where α is the degree of conversion, τ is the time, k_1, k_2 and k_3 are the reaction rate constants, and n is a constant.

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Table 1b. Results of measurements at temperatures 350-540 °C (I series)

τ min.	$\dfrac{\sqrt{\tau}}{2,3}$	Temperatura 455 °C Temperature			Temperatura 498 °C Temperature			Temperatura 520 °C Temperature			Temperatura 540 °C Temperature		
		w_τ	$\lg\left(\dfrac{w_0}{w}\right)$	k_3	w_τ	$\lg\left(\dfrac{w_0}{w}\right)$	k_3	w_τ	$\lg\left(\dfrac{w_0}{w}\right)$	k_3	w_τ	$\lg\left(\dfrac{w_0}{w}\right)$	k_3
5	0,97	0,7606	0,0220	0,0227	0,7523	0,0265	0,0273	0,7489	0,0286	0,0295	0,7416	0,0331	0,0341
10	1,37	0,7430	0,0315	0,0229	0,7284	0,0167	0,0296	0,7200	0,0457	0,0332	0,7090	0,0522	0,0380
15	1,68	0,7364	0,0395	0,0235	0,7157	0,0183	0,0287	0,6996	0,0584	0,0347	0,6801	0,0705	0,0420
20	1,94	0,7295	0,0463	0,0208	0,7054	0,0346	0,0281	0,6898	0,0645	0,0332	0,6681	0,0795	0,0409
25	2,17	0,7242	0,0433	0,0198	0,6931	0,0611	0,0281	0,6813	0,0697	0,0321	0,6520	0,0888	0,0408
30	2,37	0,7200	0,0457	0,0193	0,6880	0,0656	0,0276	0,6701	0,0766	0,0323	0,6490	0,0906	0,0382
35	2,57	0,7151	0,0487	0,0189	0,6807	0,0701	0,0272	0,6611	0,0809	0,0323	0,6444	0,0941	0,0366
40	2,75	0,7111	0,0511	0,0186	0,6759	0,0734	0,0268	0,6558	0,0864	0,0315	0,6442	0,0962	0,0350
45	2,92	0,7068	0,0539	0,0185									
		$k_{3śr} = 0,0206$ błąd średni 8,3 % mean error			$k_{3śr} = 0,0280$ błąd średni 2,45 % mean error			$k_{3śr} = 0,0325$ błąd średni 3,25 % mean error			$k_{3śr} = 0,0383$ błąd średni 6,9 % mean error		

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Equation 1, given by Spencer and Topley (3), (14), describes the rate of displacement of the substrate-product solid interface (reaction boundary) in the kinetic range of the reaction. Equation 2, cited by Pavluchenko (5), describes the rate of displacement of the substrate-product solid interface in the diffusion range of the reaction. Equation 2 is valid of the process takes place in a semi-infinite or infinite space and is associated with an irreversible chemical reaction. If the diffusion space cannot be approximately considered semi-infinite (or infinite), the power exponent of τ can take different values in the range from 0.5 to 1 (6).
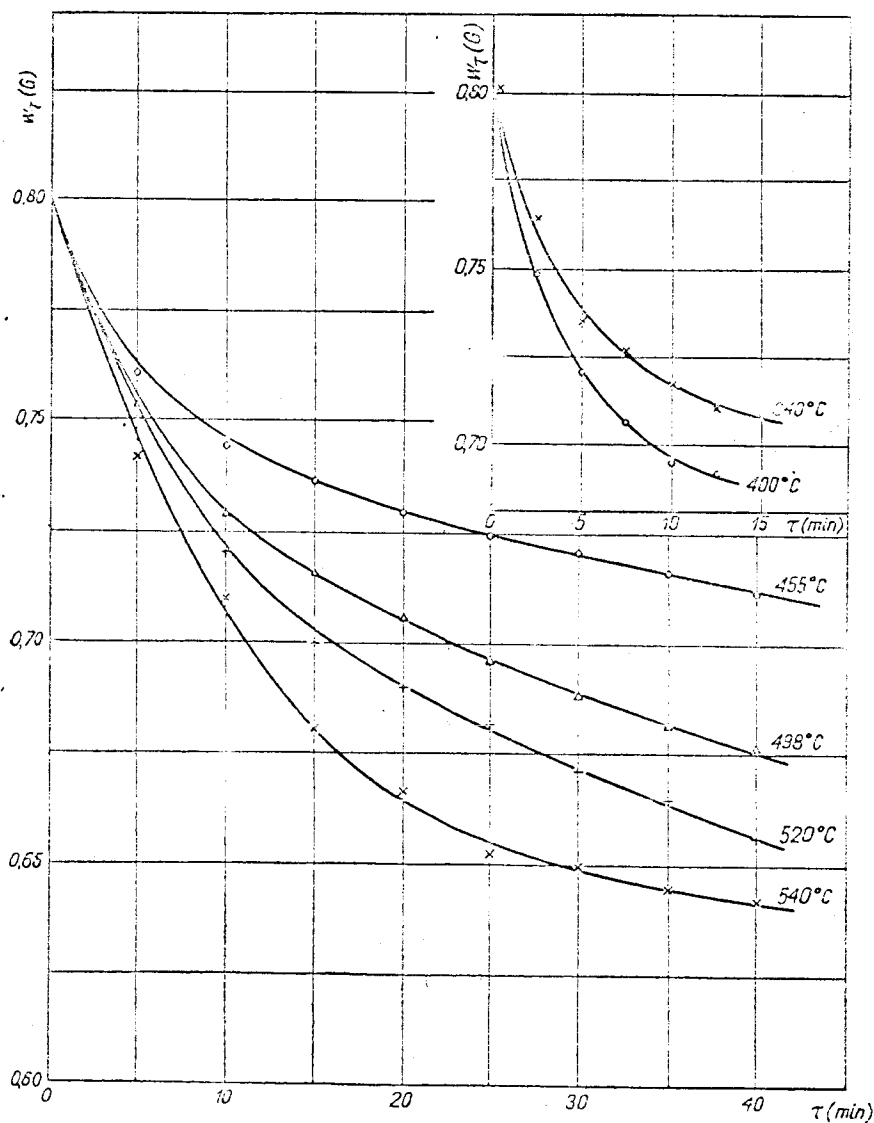
Figure 1. Results of experiments at temperatures 300-540°C (I series of measurements); decomposition of basic ammonium aluminum sulphate.
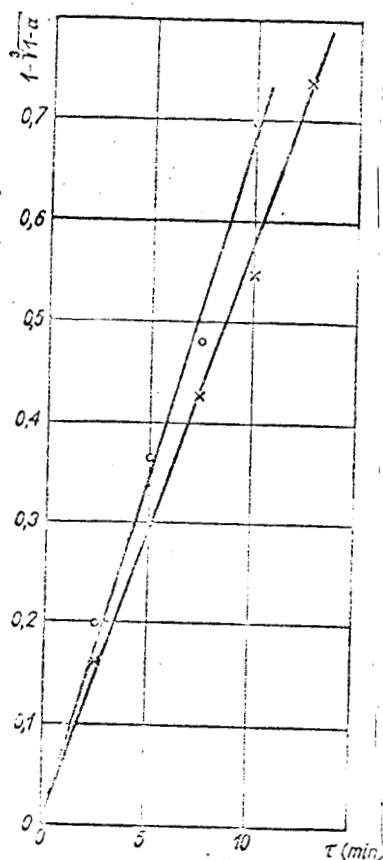
Figure 2. Displacement rate of the substrate-product solid interface in the kinetic range of reaction; decomposition of basic ammonium aluminum sulphate.

Equation 3 was derived by Avrami (7),(8), Kolmogorov (9) and Yerofeyev (10) for reactions proceeding in the range of formation of nuclei of the new phase. This equation is identical in form to that obtained empirically by Kazayev (11) and used for describing various reactions.

According to Roginskiy and Todes (12), from an equation of the general type of relation (3), a first-order reaction rate equation (n = 1) is obtained when the rate of constant of the reaction, as a result of which the reacting surface moves into the body of the crystal, is much greater than the rate of formation of nuclei of the new phase. According to Kazayev (11), n is close or equal to 0.5 if the process takes

Table 2a. Results of measurements at 430°C

τ min.	$\sqrt{\tau}$	w_τ	$1-\sqrt[3]{1-a}$	k_2
5	2,23	0,7865	0,635	0,0157
7,5	2,74	0,7829	0,643	0,0168
10	3,16	0,7814	0,650	0,0158
12,5	3,54	0,7786	0,657	0,0161

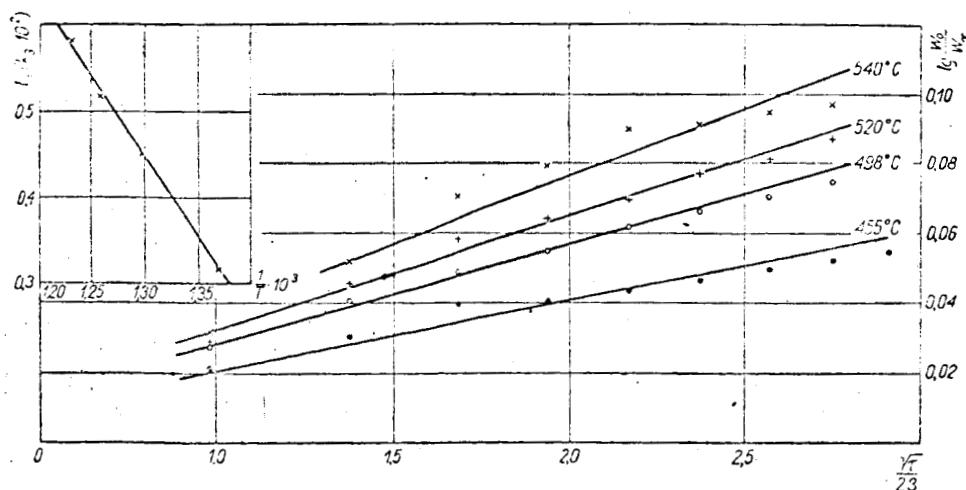$$k_{2cr} = 0,0163$$
mean error $\left| 2,75 \right. \%$

Figure 3. Values of constants k_3 and empirical dependence of k_3 on temperature; decomposition of basic ammonium aluminum sulphate.

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Table 2b. Results of measurements at temperatures 470-540°C (II series)

τ min.	Temperatura 470°C Temperature			Temperatura 495°C Temperature			Temperatura 542°C Temperature		
	w_τ	$1-\sqrt[3]{1-a}$	k_1	w_τ	$1-\sqrt[3]{1-a}$	k_1	w_τ	$1-\sqrt[3]{1-a}$	k_1
5	0,7839	0,043	0,0086	0,7792	0,056	0,0112	0,7611	0,111	0,0222
10	0,7765	0,064	0,0064	0,7656	0,103	0,0103	0,7129	0,300	0,0300
15	0,7692	0,086	0,0057	0,7504	0,147	0,0098	0,6843	0,515	0,0343
20	0,7633	0,104	0,0052	0,7396	0,187	0,0094	0,6733	0,693	0,0346
25	0,7560	0,128	0,0051	0,7311	0,222	0,0089	0,6694	—	—
30				0,7243	0,251	0,0084			
35				0,7173	0,277	0,0079			

$k_{1śr} = 0,0056$ $k_{1śr} = 0,0091$ $k_{1śr} = 0,0336$

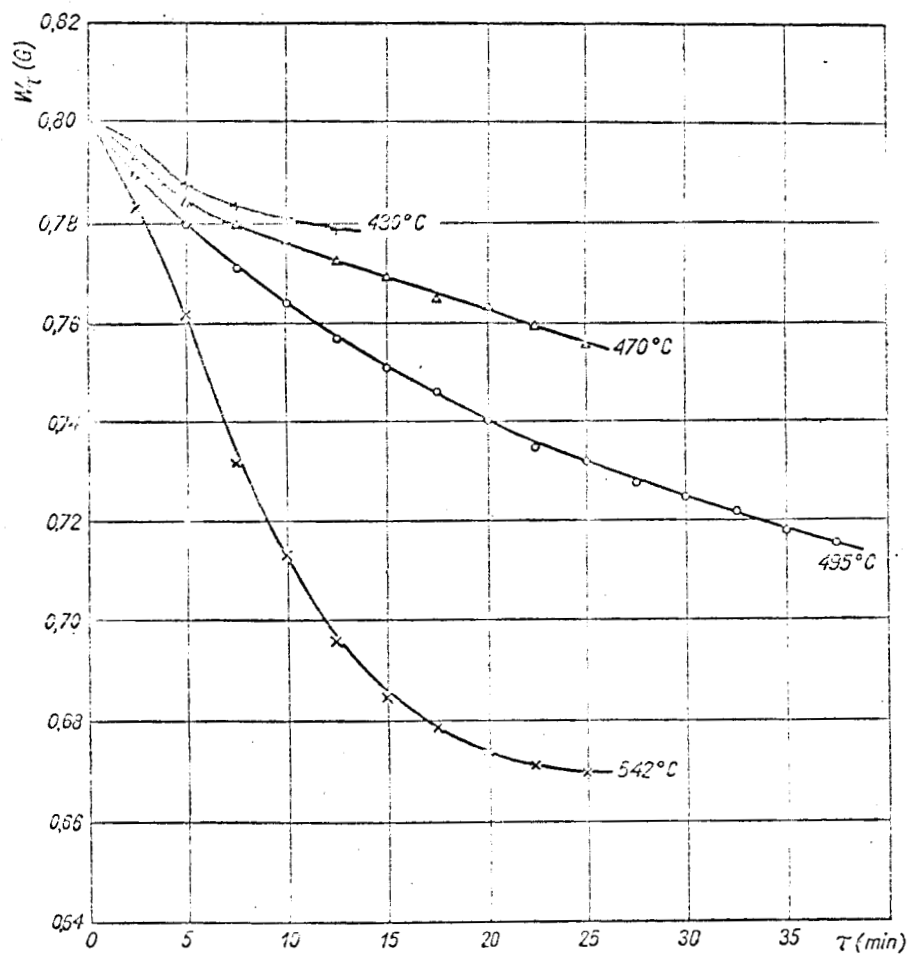mean error 8,05%   mean error 7,1%   mean error 6,3%

Figure 4. Results of experiments at 400-540°C (II series of measurements); decomposition of previously dehydrated basic ammonium aluminum sulphate.
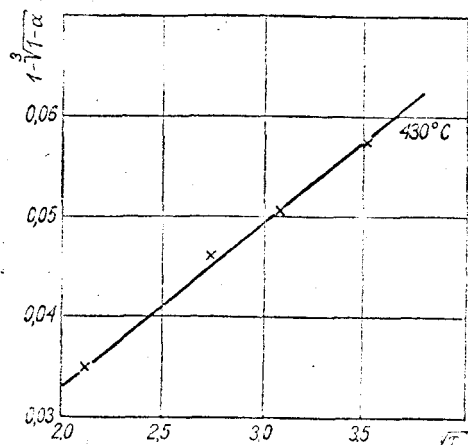
.Figure 5. Displacement rate of the substrate-product solid interface in the diffusion range of the reaction; decomposition of previously dehydrated basic ammonium aluminum sulphate.

place in the diffusion range. Other researchers (5) found that when n = 0.63, equation (3) becomes a second-order reaction-rate equation.

Equation 1 was used to process the results of measurements of the dissociation rate of basic ammonium aluminum sulphate carried out at 340 and 400°C /143 (Table 1a), while the experiments carried out 455, 498, 520 and 540°C were processed by means of equation 3 converted into the form:

$$w_\tau = w_0 \exp\left(-k_3 \tau^{0,5}\right),$$

where w_τ is the weight of the sample after the time elapsed, and w_0 is the initial weight of the sample.

The power exponent n was taken (on the basis of experiments) as 0.5 (Table 1b).

The agreement of the value of n with that given by Kazayev for reactions occurring in the diffusion range is undoubtedly accidental.

The results of the calculations adequately satisfy the proposed empirical dependence (3). However, a steady although slight decrease of the values of constants k_3 with time is observed. On the basis of calculations carried out in accordance with   (3), the apparent activation energy was determined to be 8.7 kcal per mole, and the temperature dependence of constant k_3 and of the reaction rate were found to be:

$$k_3 = 7,32 \exp\left(-\frac{8,6 \cdot 10^3}{RT}\right),$$

$$w_\tau = w_0 \exp\left(-7,32 e^{-\frac{8,6 \cdot 10^3}{RT}} \cdot \sqrt{\tau}\right),$$

where T is the temperature in °K and R is the gas constant.

Both empirical relations were fulfilled in the 450-540°C range.

In order to eliminate the effect of the separation of water in the first stage of the decomposition (at temperatures up to 320°C), measurements were made on the dissociation rate of basic ammonium aluminum sulphate subjected to a preliminary dehydration.

Values of k_1 closest to constant ones were obtained when the caluclations of the results of the experiments carried out at 470, 495 and 542°C were made by using relation (1) Table 2b), and those of the experiment carried out at 430°C, by means of equation (2) Table 2a).

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On the basis of results of the experiments cited above, one can conclude that the course of the thermal dissociation of basic ammonium aluminum sulphate in the 300-540°C temperature range occurs as follows:

At 300-400°C, the overall dissociation rate of the compound is determined by the rate of the chemical reaction occurring according to the equation: /145

$$(NH_4)_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 8H_2O \rightarrow 2H_2O + (NH_4)_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O.$$

Starting at about 400°C, the joint evolution of the remaining amount of water and ammonia begins. At 400-470°C, the reaction proceeds in the diffusion range. This is indicated by the results of calculations shown in Tables 2a and Fig. 5. The average error in the value of the rate constant of the process k_2 amounts to 2.75% (maximum error 3.7%), and consequently the proposed equation of the diffusion kinetics is fulfilled fairly closely, indi-   /146 cating that the factor exerting an inhibiting effect on the course of the reaction is the diffusion of the gaseous reaction products through the growing layer of the solid product.

A further temperature increase causes the process of removal of ammonia and water to shift from the diffusion range to the kinetic range, and the results of experiments carried out at temperatures above 470°C adequately fulfill
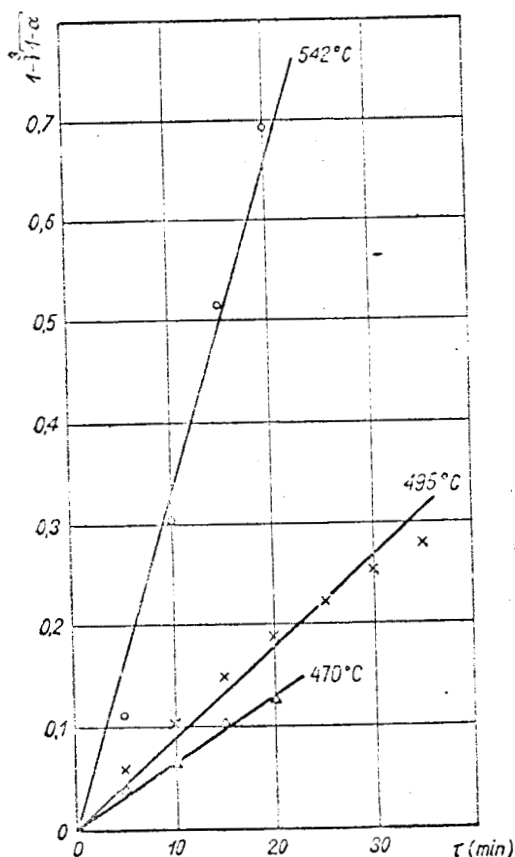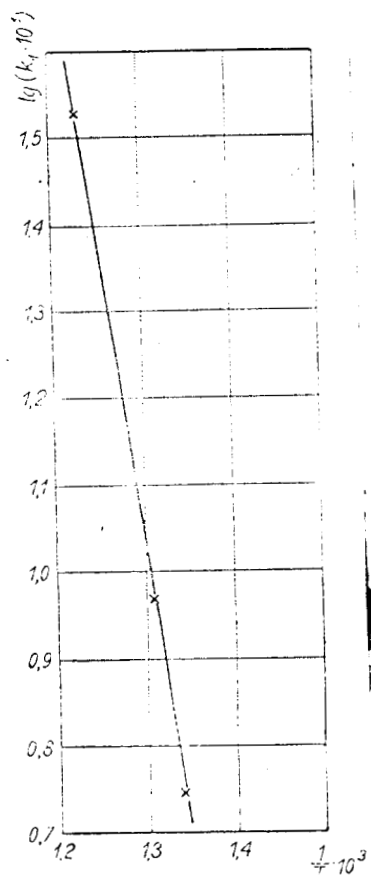

Figure 6.

Figure 7.

equation (1), which is valid for the kinetic range. Resistances to diffusion no longer have a distinctly inhibiting effect on the course of the process, probably because the decomposition pressure of the system substantially exceeds the external pressure.

The experiments showed (see Fig. 4) that the decomposition rate of previously dehydrated basic ammonium aluminum sulphate is moderate at first. As the reaction proceeds, it increases, goes through a maximum and decreases again.

This frequently observed phenomenon results from a gradual increase in the surface of contact of the two solid phases as the reaction proceeds. The observed maximum of the dissociation rate probably occurs when the magnitude of the contact surface between the phases is greatest, i.e., when the entire surface of the substrate is covered with a layer of solid product. This assumption is confirmed by calculations given as an example in Table 4. The high values of constants k_1 in the initial period of the experiment indicate the formation of new reaction centers (nuclei of the new phase), this being associated with an increase in the contact surface of the solid phases on which most of the reaction takes place, and hence, with an increase of the decomposition rate.

On the basis of the experiments carried out at 470, 495 and 542°C (partially dehydrated basic ammonium aluminum sulphate, Table 2b) the value of the apparent activation of energy was determined to be 32.7 kcal per mole. This value being known, the temperature dependence of the reaction rate constant was determined: /147

$$k_1 = 1,78 \cdot 10^7 \exp\left(-\frac{16,33 \cdot 10^3}{T}\right)$$

The temperature dependence of the reaction rate was also determined:

$$1 - \sqrt[3]{1-a} = 1,78 \cdot 10^7 \exp\left(-\frac{16,33 \cdot 10^3}{T}\right) \cdot \tau.$$ /148

Table 3a. Results of measurements at temperatures 750-833°C (III series)

τ min.	$\sqrt{\tau}$	Temperatura 784°C Temperature			Temperatura 815°C Temperature			Temperatura 833°C Temperature		
		w_τ	$1-\sqrt[3]{1-a}$	k_2	w_τ	$1-\sqrt[3]{1-a}$	k_2	w_τ	$1-\sqrt[3]{1-a}$	k_2
20	4,47							0,2310	0,278	0,0623
25	5,00				0,2328	0,273	0,0547	0,2368	0,326	0,0652
30	5,47				0,2242	0,311	0,0568	0,2211	0,393	0,0719
35	5,91	0,2855	0,178	0,0301	0,2261	0,359	0,0608	0,2087	0,458	0,0775
40	6,32	0,2795	0,195	0,0309	0,2185	0,400	0,0643	0,1997	0,517	0,0819
45	6,70	0,2724	0,213	0,0318	0,2109	0,446	0,0666	0,1954	0,550	0,0822
50	7,07	0,2674	0,227	0,0321	0,2057	0,477	0,0674			
55	7,41	0,2619	0,245	0,0331	0,2011	0,509	0,0687			
60	7,74	0,2571	0,255	0,0333	0,1993	0,521	0,0674			

$k_{2śr} = 0,0319$	$k_{2śr} = 0,0635$	$k_{2śr} = 0,0735$
błąd średni < ±5 %	błąd średni ±5 %	błąd średni ±10 %
mean error	mean error	mean error

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τ min.	Temperatura 860°C Temperature			Temperatura 896°C Temperature		
	w_τ	$1-\sqrt[3]{1-a}$	k_1	w_τ	$1-\sqrt[3]{1-a}$	k_1
2,5				0,2963	0,151	0,0604
5	0,2831	0,200	0,0400 *	0,2490	0,284	0,0508
7,5	0,2574	0,258	0,0344 *	0,2128	0,436	0,0581
10	0,2423	0,307	0,307	0,1916	0,586	0,0586
12,5	0,2211	0,393	0,315	0,1821	0,716	0,0477 *
15	0,2064	0,472	0,315	0,1778	—	—
17,5	0,1966	0,542	0,310			
20	0,1880	0,627	0,314			

$k_{1sr} = 0,0312$	$k_{1sr} = 0,0585$
mean error 0.95 %	mean error 1.74 %
maximum error 1.6 %	maximum error 3.2 %

Both relations are valid in the 470-540°C range.

Equations (1) and (2) were used to process the results of experiments on the decomposition rate of the preparation studied in series III of the experiments. Results of experiments carried out at 860 and 896°C satisfy relation (1) very closely. The average relative error does not exceed 1.75%, and the maximum error is ±3.2%. /149
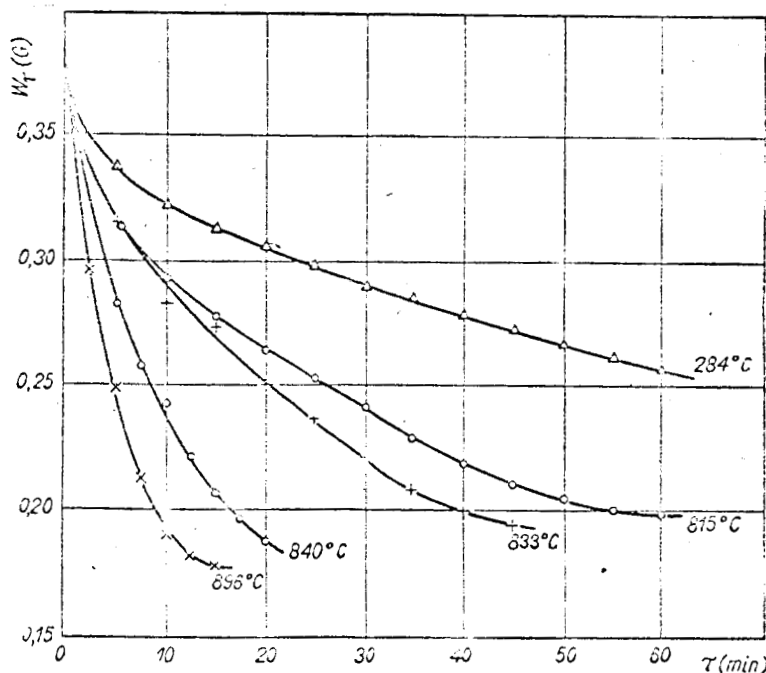

Figure 8. Results of measurements at 750-900°C (III series); decomposition of preparation of the formula $3Al_2O_3 \cdot 4SO_2$.

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From the calculations collected in Table 3b it may be concluded that the decomposition at 860 and 896°C takes place in the kinetic range. Resistances to diffusion did not have a distinct effect on the course of the reaction, probably because at high temperatures the decomposition pressure of the system substantially exceeds the external pressure. At the same time, the system is far below the melting point of Al_2O_3, and the lack of sintering of the solid reaction product facilitates the diffusion of gaseous products.

During the dissociation of preparation III at 784, 815 and 833°C, the superposition of several processes is observed. Table 5 illustrates the values of constants k_1 and k_2 calculated according to relations (1) and (2) for 815°C.

The high values of k_1 in the initial period of the dissociation indicate formation of new reaction centers; this is undoubtedly the period during which nuclei of the new phase are formed. The succeeding values of k_1 decrease slowly, and hence the reaction takes place mainly on the contact surface of the phases in accordance with equation (1).

Results of experiments carried out at 784, 815 and 833°C were processed by means of equation (2). The calculations indicate a constancy of the values of k_2 within ±5%, and only for the temperature of 833°C does k_2 change over wider limits (±10%).

The satisfactory constancy of the values of k_2 calculated from equation (2) indicates that the factor retarding the reaction at temperatures below 860°C is the phenomenon of diffusion of gaseous decomposition products through the layer of grains of the solid reaction product (Al_2O_3), which grows on the surface of the dissociating substrate.
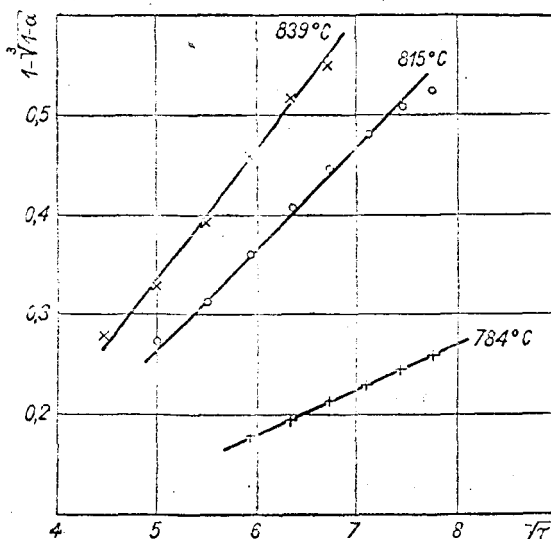

Figure 9. Displacement rate of the substrate-product solid interface in the diffusion range of the reaction; decomposition of preparation of the formula $3Al_2O_3.4SO_3$.

However, diffusion probably is not a process much slower than the kinetic process, i.e., than the dissociation, and for this reason a slow increase of k_2 was observed.

The values of the apparent activation energy for the diffusion and kinetic range of the reaction are respectively 45.7 and 63.0 kcal per mole and characterized the temperature dependence of the reaction rate constant.

The following values were found: for the diffusion range (780-860°C):

$$k_2 = 1{,}18 \cdot 10^7 \exp\left(-\frac{22{,}9 \cdot 10^3}{T}\right)$$

and

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and

$$1 - \sqrt[3]{1-a} = 1{,}18 \cdot 10^7 \exp\left(-\frac{22{,}9 \cdot 10^3}{T}\right) \cdot \sqrt{\tau},$$

and for the kinetic range (860-900°C):

$$k_1 = 3{,}86 \cdot 10^{10} \exp\left(-\frac{31{,}5 \cdot 10^3}{T}\right)$$

and

$$1 - \sqrt[3]{1-a} = 3{,}86 \cdot 10^{10} \exp\left(-\frac{31{,}5 \cdot 10^3}{T}\right) \cdot \tau.$$

The relatively minor difference in the values of apparent activation energies obtained indicates that the range of the course of the reaction described by diffusion equation 2 is actually a transition range.
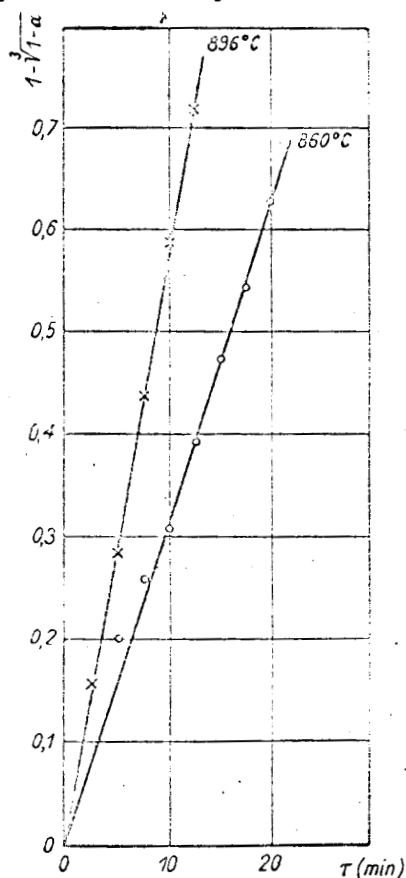

Figure 10. Displacement rate of the solid interface substrate--product in the kinetic reaction range; decomposition of preparation of the formula 3Al$_2$O$_3$.4SO$_3$.
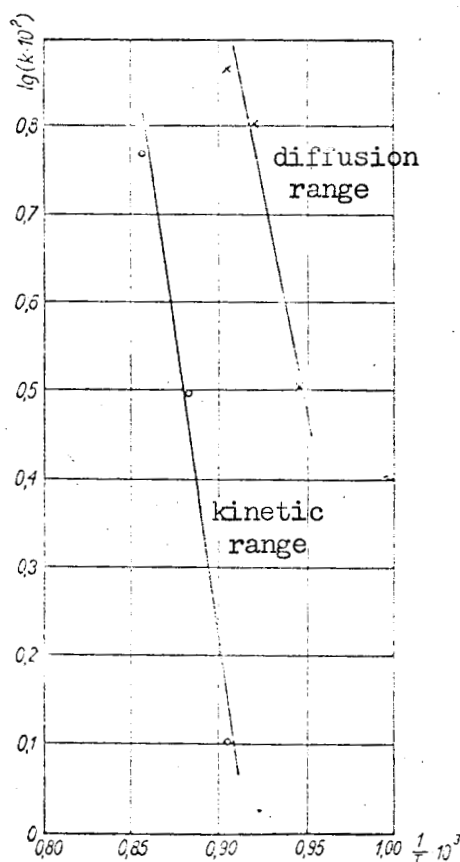
Figure 11. Dependence of reaction rate constants k_1 and k_2 on the temperature in diffusional and kinetic reaction range; decomposition of preparation of the formula 3Al$_2$O$_3$.4SO$_3$.

The value of the apparent activation energy found for the kinetic range (63.0 kcal per mole) is much lower than the value of the heat of reaction calculated from thermomechanical data (87.56 kcal per mole).

Table 4. Values of the reaction rate constants calculated according to formulas (1) and (2). 1st decomposition rate

$t°C$	τ min.	5	7,5	10	12,5	15	20	25	30	35
430	k_1	0,0070	0,0061	0,0050	0,0046	—	—	—	—	—
	k_2	0,0157	0,0168	0,0158	0,0161	—	—	—	—	—
495	k_1	0,0112	—	0,0103	—	0,0098	0,0094	0,0089	0,0084	0,0079
	k_2	0,0251	—	0,0326	—	0,0350	0,0418	0,0444	0,0459	0,0469

Table 5. Values of the reaction rate constants calculated according to formulas (1) and (2); temperature 515°C

τ min.	5	10	15	20	25	30
$\sqrt{\tau}$	2,23	3,16	3,87	4,47	5,00	5,47
k_1	0,0226	0,0160	0,0132	0,0119	0,0105	0,0104
k_2	0,0507	0,0507	0,0512	0,0530	0,0547	0,0568

The activation energy is equal to the heat of reaction at a considerable distance from the state of equilibrium (13). In the temperature range observed, the activation energy obtained is less than the heat of reaction probably because the range in which the reaction occurs is close to the diffusion range. Not enough data are available, however, to elucidate this phenomenon completely.

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